Interrelationship of Macropores and Subsurface Drainage for Conservative Tracer and Pesticide Transport

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ABSTRACT

Macropore flow results in the rapid movement of pesticides to subsurface drains, which may be caused in part by a small portion of macropores directly connected to drains. However, current models fail to account for this direct connection. This research investigated the interrelationship between macropore flow and subsurface drainage on conservative solute and pesticide transport using the Root Zone Water Quality Model (RZWQM). Potassium bromide tracer and isoxaflutole, the active ingredient in BALANCE herbicide [(5-cyclopropyl-4-isoxazolyl) [2(methylsulfonyl)-4-(trifluoromethyl)phenyl] methanone], with average half-life of 1.7 d were applied to a 30.4-ha Indiana corn (*Zea mays* L.) field. Water flow and chemical concentrations emanating from the drains were measured from two samplers. Model predictions of drain flow after minimal calibration reasonably matched observations (slope = 1.03, intercept = 0.01, and R^2 = 0.75). Without direct hydraulic connection of macropores to drains, RZWQM under predicted bromide and isoxaflutole concentration during the first measured peak after application (e.g., observed isoxaflutole concentration was between 1.2 and 1.4 μg L^{-1}, RZWQM concentration was 0.1 μg L^{-1}). This research modified RZWQM to include an express fraction relating the percentage of macropores in direct hydraulic connection to drains. The modified model captured the first measured peak in bromide and isoxaflutole concentrations using an express fraction of 2% (e.g., simulated isoxaflutole concentration increased to 1.7 μg L^{-1}). The RZWQM modified to include a macropore express fraction more accurately simulates chemical movement through macropores to subsurface drains. An express fraction is required to match peak concentrations in subsurface drains shortly after chemical applications.

Subsurface drainage is an important component of successful agricultural water management in areas with shallow ground water. Inadequate drainage can result in delayed planting and a shorter growing season, stunted plant root growth, and possibly crop failure due to excessive water stress. Drains are successful in achieving the water quantity goals of agriculture management. However, concerns exist about the rapid transport of pesticides from the soil surface through macropores. Preferential flow in macropores leads to rapid transport of pesticides to the subsurface (Magesan et al., 1995; Kladivko et al., 1999; Shipitalo and Gibbs, 2000). This rapid transport has been experimentally verified in both field and laboratory studies (Munster et al., 1995; Elliott et al., 1998; Kladivko et al., 1999; Sadeghi et al., 2000). The ability to model pesticide transport and subsurface drainage systems is important for evaluating potential environmental consequences of pesticide use. Performing field research under all of the expected conditions (soils, climate, and chemical applications) is cost prohibitive. Agriculture system models can predict chemical fate under numerous hydrologic, soil, and agricultural management practice conditions.

Pesticide movement to drains is commonly simulated with macropore flow (Chen and Wagenet, 1992; Saxena et al., 1994; Kumar et al., 1998; Villholth and Jensen, 1998; Villholth et al., 1998). However, researchers understand little about the connectivity of macropores with subsurface drainage systems. Immediate breakthrough of solutes and pesticides in subsurface drainage indicates extraordinarily efficient transport by preferential pathways, hypothesized to be the result of a few drain-connected macropores by Villholth et al. (1998) and Shipitalo and Gibbs (2000). A field study in Ohio indicated that macropores created by earthworm burrows directly transfer water to subsurface drains (Shipitalo and Gibbs, 2000). Infiltration rate correlated to distance from the subsurface drains: the rate at which water entered earthworm burrows declined with the log of distance from the subsurface drains. Direct transfer of water was limited to a distance of 0.5 m on either side of the drain (Shipitalo and Gibbs, 2000). A field and modeling study in Denmark observed extremely fast breakthrough of tracer generated by a few, drain-connected macropores (Villholth and Jensen, 1998).

The objective of this research is to investigate the interrelationship between preferential flow through macropores and artificial subsurface drainage on conservative tracer and pesticide transport. The Root Zone Water Quality Model (RZWQM) was used to simulate flow from a subsurface drained field in Allen County, Indiana, after application of potassium bromide (KBr) tracer and isoxaflutole (ISO), the active ingredient in BALANCE herbicide, during the 2000 growing season. This research evaluates RZWQM's ability to predict chemical transport to subsurface drains using minimal calibration and proposes a modification to RZWQM to account for macropores directly connected with subsurface drains.

MATERIALS AND METHODS

The RZWQM is a commonly applied model for water flow and pesticide transport from agricultural fields. It is a one-dimensional (vertical) model that simulates physical, chemical, and biological processes of a unit area of an agricultural crop production system. The RZWQM simulates plant growth and

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Abbreviations: EF, express fraction; ISO, isoxaflutole; MUUF, map unit use file soil database; NOF, normalized objective function; RZWQM, Root Zone Water Quality Model.

the movement of water, nutrients, and pesticides in surface runoff, through the soil profile, and into ground water. The model divides water flow processes into two phases: (i) infiltration into the soil matrix and macropores with macropore–matrix interaction, and (ii) redistribution of moisture in the soil matrix (Ahuja et al., 2000).

The Green and Ampt (1911) equation is used to calculate infiltration rates into the soil profile. The model simulates subsurface drainage using the integrated Hooghoudt equation developed by Bouwer and van Schilfgaarde (1963). This equation predicts the rate of fall of the water table in relation to the subsurface drain:

$$\frac{Kt}{f} = \frac{CL^2}{8D_e}\ln\left[\frac{m_o(m_t + 2D_e)}{m_t(m_o + 2D_e)}\right] \quad [1]$$

where K is the hydraulic conductivity of the soil (cm s^{-1}), D_e is the effective depth of the impermeable layer below the drain center (cm), t is time (s), L is the distance between the drains (cm), f is the drainable pore-space; C is a coefficient relating the fall midway between the drains to the average fall of the water table; and the variables m_o and m_t are the initial value and value at time t of the height of the water table above drain centers midway between drains (cm). The model uses modified Brooks-Corey relationships (Brooks and Corey, 1964) for the unsaturated hydraulic conductivity, $K(h)$ (cm s^{-1}) vs. matric suction head, h (cm), and the soil water content, θ, vs. h relationships:

$$K(h) = C_1|h|^{-N_1} \qquad h \leq S$$
$$K(h) = C_2|h|^{-N_2} \qquad h > S \quad [2]$$

$$\theta = \theta_s - A_1|h| \qquad h \leq S$$
$$\theta - \theta_r = B|h|^{-A_2} \qquad h > S \quad [3]$$

where S is the bubbling pressure (cm), A_2 is the pore size distribution index, N_2 is the exponent for the conductivity curve, C_1 is the saturated hydraulic conductivity (cm s^{-1}), θ_r is the residual water content (cm^3 cm^{-3}), θ_s is the saturation water content (cm^3 cm^{-3}), C_2 is the second intercept on the conductivity curve, N_1 is the first exponent on the conductivity, and B is given by the following expression:

$$B = (\theta_s - \theta_r - A_1 S)S^{A_2} \quad [4]$$

The model routes precipitation that exceeds the infiltration rate into macropores based on a flow capacity limit determined by Poiseuille's law (Malone et al., 2003). The model then evenly distributes water entering into macropores among the number of effective macropores per unit area:

$$nmacro^* = \frac{macro^*}{\pi r_p^2} \quad [5]$$

The volume of effective macropores per unit volume of soil is *macro** (cm^3 cm^{-3}), as defined in detail by Malone et al. (2003), and r_p is the average macropore radius (cm). Flow is sequentially routed downward through continuous macropores in 1-cm increments and allowed to laterally infiltrate into surrounding, unsaturated soil based on a radial infiltration rate in macropores. This radial infiltration rate is dependent on a lateral sorptivity reduction factor that represents impedance of infiltration by organic material on macropore walls or macropore wall compaction (Malone et al., 2001).

The RZWQM simulates chemical transport through a variety of mechanisms. Rainfall transports chemicals from the soil to overland flow. The model simulates chemical washoff from plant foliage and mulch. The RZWQM routes water and chemicals through macropores and allows reactions through chemical partitioning with soil surrounding the macropores. The model assumes a linear isotherm between chemical adsorbed to soil and chemical in solution (Malone et al., 2001).

Field Experiments

The research site was a 30.4-ha isolated field located in Maumee Township, Allen County, Indiana, approximately 1.6 km east of the town of Woodburn (Fig. 1). The field consists of Hoytville silty clay (fine, illitic, mesic Mollic Epiaqualfs) with slope less than 2%. The field contained systematic subsurface drain lines (polyurethane pipes) with a 10-m spacing running east–west that connect to a drain system emptying at the northeast and southeast corners of the field. The subsurface drains were at a depth of 0.9 to 1.2 m. No-till agricultural management practices were used at the site. Crop history records indicate that corn was planted at the test site during 1998, followed by soybean [*Glycine max* (L.) Merr.] in 1999, and then corn again in 2000.

A weather station adjacent to the field recorded hourly temperature, relative humidity, solar radiation, wind speed and direction, and rainfall during the 2000 growing season. Table 1 illustrates the average local rainfall for the field experiment months along with the average minimum and maximum air temperatures. Figure 2 presents the observed daily rainfall at the research site. Soil samples were collected every 15 cm from the soil surface to approximately 1.5 m below the soil surface. Particle-size distribution, organic matter content, and bulk density were estimated from the core samples collected on site (Table 2).

The field was uniformly treated with potassium bromide (KBr) at a rate of 39.6 kg ha^{-1} on 29 Apr. 2000. The tracer was dissolved in water and sprayed in a uniform broadcast application over the field. Isoxaflutole (ISO), the active ingredient in BALANCE herbicide, was applied at the rate of 0.13 kg ha^{-1} to the field 5 d after application of the KBr tracer. Isoxaflutole is a selective herbicide for control of certain broadleaf and grass weeds in field corn (Pallett et al., 1998). It can be used as a preplant (surface-applied or incorporated) or preemergence herbicide, and can be used in conventional, conservation tillage, or no-till tillage systems. Physicochemical and environmental fate properties for ISO are summarized in Table 3.

Soil samples were collected periodically (days of the year 125, 132, 139, 155, and 186) during 6 mo following application to quantify the distribution of bromide (Br) and ISO within the soil profile. Core samples were obtained to a depth of 1.82 m. The field was divided into four quadrants and sampling locations were selected using a random number generator. Cores were collected using the bucket-auger technique. Cores from only the top 15 cm were collected for the first 5 d after the tracer application. On subsequent samplings, the entire soil profile was sampled and cores within a quadrant were composited.

Drain flow was measured using an Isco Model 730 Bubble Flow Meter (Isco, Lincoln, NE). The level of water in the subsurface drains and flow was determined based on the pipe diameter, smoothness, and slope. Flow data were missing for high-flow events due to flooding of the sampling site. Therefore, available flow data were the regression limbs of subsurface drainage after storm events. Multiple water samples from the subsurface drains were collected daily starting 5 d after KBr application for the duration of the growing season. The water and soil samples were analyzed to determine the extent of leaching to the drainage system. The drain sampling points were selected where the subsurface drain systems empty into

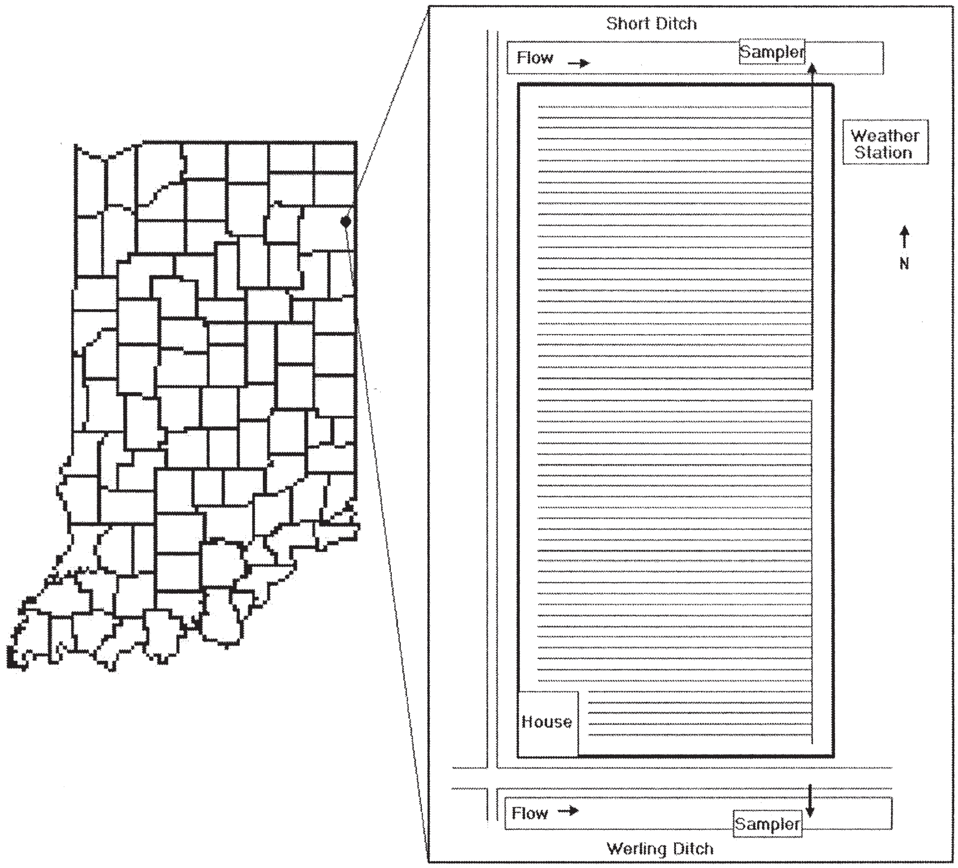


Fig. 1. Location and depiction of bromide (Br) and pesticide transport field experiment in Allen County, Indiana.

the collector ditches. The drain outlets were modified to allow use of an automated sampling device. A sample pickup was placed where the drains were first exposed at the ditch bank. An Isco model 6700 sampler (Isco, Lincoln, NE) was installed at each drain and programmed to collect a water sample every 80 min (18 samples every 24-h period). Each day the filled sample bottles were collected and new empty bottles placed in the automated sampler. The freshly collected samples were labeled, dated, and placed in frozen storage.

Tracer samples were analyzed using an ion chromatograph (USEPA, 1993). Soil samples were extracted with 100 mL of HPLC-grade water after thawing and then centrifuged. An aliquot of the extract was then diluted with HPLC-grade water before analysis by ion chromatography. The limit of detection of the method is 0.1 mg L^{-1}. Water samples were analyzed for residues of isoxaflutole using a liquid chromatography/mass spectrometry system (Smitley et al., 2000). The limit of quantification is 0.010 $\mu g\ L^{-1}$. The limit of detection is 0.003 $\mu g\ L^{-1}$. Samples were fortified with 13C labeled standards of the three analytes. Residues of isoxaflutole were extracted from water using a RP-102 resin cartridge (Applied Separations, Allentown, PA), and then removed with acetonitrile–methanol. All residue analysis was accomplished by LC-MS-MS (Applied Separations, Allentown, PA) using a C-8 column.

Table 1. Historical meteorological conditions for Allen County, Indiana.

Parameter	May	June	July	August
Avg. min. air temp., °C	10.2	15.9	17.3	16.5
Avg. max. air temp., °C	21.7	26.9	29.5	28.4
Total monthly rainfall, cm	9.74	10.59	8.56	7.72

The typical analytical set included 4 to 20 field samples, at least one untreated control sample and at least one fortified procedural recovery sample. Each set of sample injections was bracketed by calibration standard injections of appropriate analyte concentrations.

RZWQM Modeling

The soil profile was divided into five layers for input into RZWQM: 0 to 15 cm, 15 to 30 cm, 30 to 107 cm, 107 to 152 cm,

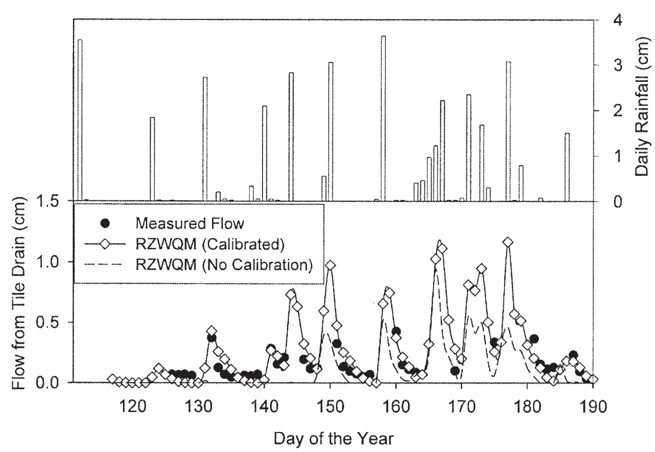


Fig. 2. Daily rainfall and time series comparison of observed vs. predicted water flow from the subsurface drains using default Root Zone Water Quality Model (RZWQM) soil parameters (no calibration) and calibrated conductivity and Brooks-Corey parameters (calibrated).

Table 2. Measured soil types, percentage organic content, and bulk density by depth for the field site in Allen County, Indiana.

Layer	Depth	Soil type	% Organic matter	Bulk density
	cm			g cm^{-3}
1	15	clay	3.02	1.17
2	30	clay	2.73	1.18
3	107	clay	1.10	1.18
4	152	clay	0.83	1.17

and 152 to 296 cm. The model was capable of deriving critical soil hydraulic parameters (i.e., porosity, conductivity, field capacity, and water retention parameters) based on minimum input of the particle-size distribution and bulk density. Therefore, particle-size distribution and bulk density from the soil samples were input into the model to generate a first estimate of the soil properties. These soil samples suggested a uniform soil property distribution with depth in the profile. Additional soil parameters were available from the Map Unit Use File (MUUF) soil database (Baumer et al., 1987; Rawls et al., 2001) for Hoytville silty clay. Soil hydraulic data can be generated by MUUF for use in different hydrologic–water quality simulation models. Data from the soil database compared reasonably well to laboratory measurements of soil texture, organic matter, and bulk density from the field samples. The surface crust conductivity and soil macroporosity parameters including the macropore radius, effective macroporosity, and lateral sorptivity reduction factor were obtained from selected literature. The same macropore parameters were input for all depths. Management practices for the field were entered into the model including the applications of KBr and ISO. Weather data were input based on measured hourly data from the weather station.

The model was calibrated by adjusting the modified Brooks-Corey parameters (Brooks and Corey, 1964), vertical saturated conductivity, and lateral saturated conductivity until model predictions matched observed subsurface drainage collected during the experiments from Day 120 to 190 of the 2000 growing season. Potassium bromide transport through the soil matrix and macropores was then simulated. The current released version of RZWQM simulated macropore flow to cease at the water table. Therefore, the model assumed no connection between macropores and subsurface drains. The RZWQM was modified to include a contributing area parameter, or express fraction, relating the percentage of macropores in direct hydraulic connection to subsurface drains. Observed Br concentrations were compared with predicted concentrations both before and after model modification. Model evaluations were based on linear regressions of predicted vs. measured subsurface drainage and concentrations. An additional test based on an acceptance criterion as quantified by a normalized objective function (NOF) was utilized (Hession et al., 1994; Kornecki et al., 1999). This function is the ratio of the standard deviation of differences (STDD) to the overall mean (X_a) of the observed parameter:

$$\mathrm{NOF} = \frac{\mathrm{STDD}}{X_a} = \frac{\sqrt{\dfrac{\sum_{i=1}^{n}(x_i - y_i)^2}{n}}}{X_a} \quad [6]$$

where x_i and y_i are the i^{th} observed and predicted values, respectively. An NOF value of <1 satisfies the site-specific criteria (Hession et al., 1994).

RESULTS AND DISCUSSION

Model Calibration

Table 4 presents parameters values derived by RZWQM. Soil hydraulic parameters were assumed uniform throughout the soil layers. Soil macroporosity parameters were not modified from their literature suggested values (Table 5). The lateral sorptivity reduction factor (0.1) is realistic compared with other RZWQM applications such as Ahuja et al. (1995) and Malone et al. (2003), which suggest a value of approximately 0.1. Effective macroporosity (0.00005) matches reported values by Malone et al. (2001). The macropore radius (0.05 cm) falls within the range of reported radii for tilled (0.03 cm) and short-term no-till (0.06 cm) soil (Malone et al., 2003). Surface crust conductivity (0.01 cm

Table 3. Physicochemical and environmental fate properties for isoxaflutole (ISO), the active ingredient in BALANCE herbicide.

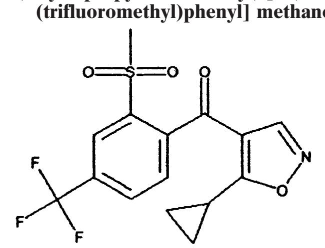
Property		Value
CAS no.		141112-29-0
Chemical name		(5-cyclopropyl-4- isoxazolyl) [2-(methylsulfonyl)-4-(trifluoromethyl)phenyl] methanone
Molecular structure		
Molecular wt., g mol^{-1}		359
Water solubility, mg L^{-1}		6.2
Octanol–water partition coefficient, log P		2.32
Vapor pressure, Pa		1.0×10^{-6} at 25°C
Soil K_{oc} at initial soil conc. (ca. 0.29 mg kg^{-1})	range	102–227
	mean ± 90% confidence interval	155 ± 35
Laboratory aerobic soil half-life, d	range	0.3–4.3
	mean ± 90% confidence interval	1.7 ± 0.9
Field dissipation half-life, d	range	0.5–3.7
	mean ± 90% confidence interval	2.0 ± 0.4
Hydrolysis half-life at pH = 7, d		0.84
Dissipation half-life from water phase in sediment–water system, d		0.5–0.6
Aquatic photolysis half-life from natural sunlight at pH = 7, d		6.7

Table 4. Default soil hydraulic parameter values derived by the Root Zone Water Quality Model (RZWQM) based on input particle-size distribution and bulk density from field measurements. Values are assumed uniform throughout the soil profile.

Parameter	Value
Vertical, saturated conductivity, C_1, cm h^{-1}	0.06
Lateral, saturated conductivity, cm h^{-1}	0.18
Bubbling pressure head, S, cm	37
Pore size distribution index, A_2	0.131
Field capacity at 0.33 bar, FC_{33}, cm^3 cm^{-3}	0.38
Field capacity at 0.10 bar, FC_{10}, cm^3 cm^{-3}	0.43
Field capacity at 15 bar, FC_{15}, cm^3 cm^{-3}	0.27
Residual soil water content, θ_r, cm^3 cm^{-3}	0.09
Saturation soil water content, θ_s, cm^3 cm^{-3}	0.48

h^{-1}) is reasonable compared with findings by McIntyre (1958) for crust conductivities of the top 5 mm of cultivated soils (0.02 cm h^{-1}) and values reported as realistic for RZWQM simulations (Malone et al., 2003).

The model significantly underpredicted subsurface drainage using these default values (Fig. 2). The model was then calibrated based on the sensitive input parameters. The model was most sensitive to Brooks-Corey parameters (Brooks and Corey, 1964), especially the bubbling pressure head and pore-size distribution index, vertical saturated conductivity, and lateral saturated conductivity. Therefore, the Brooks-Corey parameters, vertical conductivity, and lateral conductivity were adjusted until predicted subsurface drainage reasonably matched measured subsurface drainage. Field capacity values and residual and saturation water contents were not modified. The RZWQM required minimal calibration to match the observed hydrologic response of the system. Figure 2 presents a comparison of predicted vs. observed subsurface drainage. Linear regression between predicted and measured flow resulted in a slope of 1.03, intercept of 0.01, and R^2 = 0.75. The NOF was 0.7 for observed vs. predicted flow, suggesting that the model is reasonable for this site-specific application.

Table 5 presents the calibration values for hydraulic conductivity and Brooks-Corey parameters. Vertical, saturated conductivities were reasonable compared with the MUUF soil database that suggested hydraulic conductivities between 0.1 and 1.0 cm h^{-1}. Lateral, saturated conductivities were assumed three times greater than the vertical conductivity, similar to the default RZWQM parameters. The bubbling pressure head and particle-size distribution index in the calibrated model resemble a loam soil much more than a silty clay soil. In fact, the primary factor influencing model predictions of subsurface drainage was the bubbling pressure head, especially for the surface layer. Adequate subsurface drainage was not simulated in RZWQM without reducing the surface layer bubbling pressure head. Requiring a lower bubbling pressure head than expected follows a pattern exhibited in studies with RZWQM. For example, Malone et al. (2003) required a lower bubbling pressure head with RZWQM for the soil surface layer than measured experimentally from soil samples. Determining the validity of such parameters requires experimental verification from soil samples. These parameters were not measured during soil sample collection. An alternative verification was possible with the Rosetta model

Table 5. Selected literature, soil database, and calibrated Root Zone Water Quality Model (RZWQM) input parameters.

Parameter	Value
Lateral sorptivity reduction factor†	0.1
Effective macroporosity, cm^3 cm^{-3}†	0.00005
Macropore radius, cm†	0.05
Surface crust conductivity, cm h^{-1}†	0.01
Modified Brooks-Corey parameter, S_1, bubbling pressure, cm‡	
0–296 cm	5.0
Modified Brooks-Corey parameter, A_2, pore size distribution‡	
0–296 cm	0.05
Modified Brooks-Corey parameter, N_2‡	
0–296 cm	2.15
Saturated, vertical hydraulic conductivity, K_{sat}, cm h^{-1}‡	
0–15 cm	1.0
15–30 cm	0.5
30–107 cm	0.3
107–152 cm	0.1
152–296 cm	0.1
Saturated, lateral hydraulic conductivity, K_{lat}, cm h^{-1}‡	
0–15 cm	3.0
15–30 cm	1.5
30–107 cm	0.9
107–152 cm	0.3
152–296 cm	0.3

† Default value from the literature.
‡ Calibrated.

(Schaap and Leij, 1998), which estimated soil moisture characteristic curves and unsaturated hydraulic conductivity curves based on measured soil particle-size distribution and bulk density using the van Genuchten (1980) relationships. Predicted unsaturated hydraulic conductivity derived using the van Genuchten (1980) relationship for the soil samples compared reasonably well with the modified Brooks-Corey relationship (Brooks and Corey, 1964) based on calibrated soil parameters in RZWQM.

Model Evaluation

Figures 3 and 4 compare predicted Br and ISO concentrations for the calibrated, hydrologic model vs. the observed Br concentrations from the subsurface drains. Observed Br and ISO concentrations indicate rapid delivery of the tracer and pesticide to the subsurface

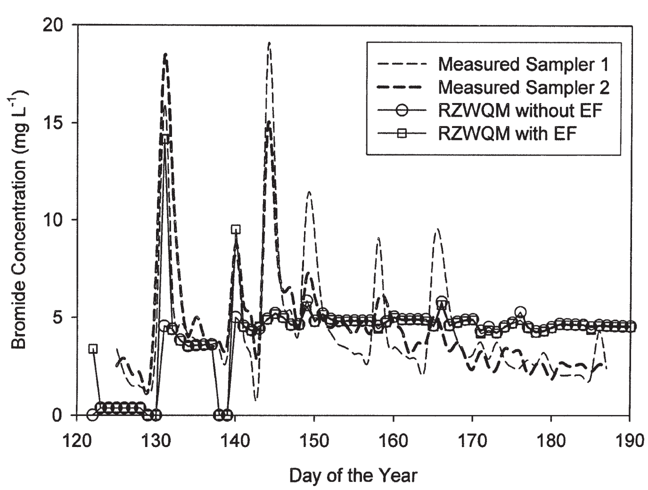


Fig. 3. Observed vs. Root Zone Water Quality Model (RZWQM) predicted bromide (Br) concentrations in the subsurface drains with the express fraction (EF) modification (RZWQM with EF) and without the express fraction (EF) modification (RZWQM without EF).

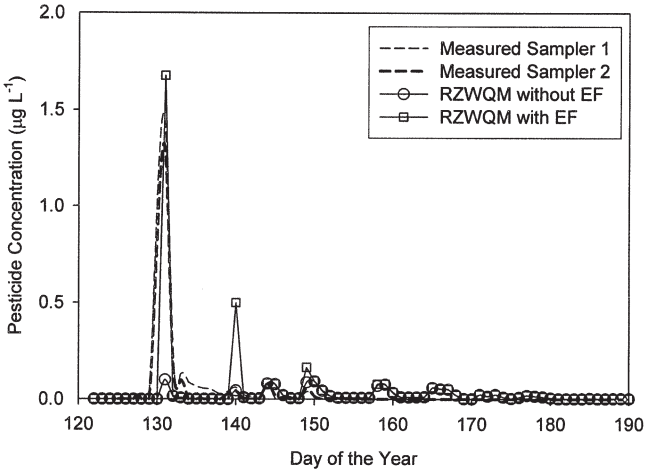


Fig. 4. Observed vs. Root Zone Water Quality Model (RZWQM) predicted isoxaflutole (ISO) concentrations in the subsurface drains with the express fraction (EF) modification (RZWQM with EF) and without the express fraction (EF) modification (RZWQM without EF).

drains. Subsurface drainage contained Br as soon as 5 d after application and ISO as soon as 3 d after application. The model met the acceptance criterion for Br (NOF = 0.8) but not ISO (NOF = 1.3). A linear regression between predicted and measured Br concentration resulted in a slope of 0.42, intercept of 1.30, and R^2 = 0.25. The model underpredicted concentrations following rainfall events soon after application of the KBr tracer. For example, observed Br concentrations in the two samplers on Day 131 ranged between 16.0 and 18.5 mg L^{-1} compared with a predicted concentration of 4.6 mg L^{-1}. The model underpredicted Br concentration relative to the average observed concentration until Day 141. The pesticide breaks down rapidly such that only one peak in concentration was observed during the study period. Concentrations in the two samplers ranged between 1.3 and 1.4 μg L^{-1} on Day 131. The model failed to capture this significant peak in predicting a concentration of approximately 0.1 μg L^{-1}. A linear regression between predicted and observed ISO concentrations resulted in a slope of <0.1.

Predicted Br concentrations in the capillary fringe and near subsurface drains were large soon after application. However, simulated concentrations of Br in subsurface drainage were not correspondingly high. Complications occurred due to difficulties in simulating chemical movement to drains because of mixing of macropore flow with saturated soil below the capillary rise depth. Hypotheses for the lack of model response to immediate Br and ISO detection in subsurface drains included the possibility of directly connected macropores as suggested by Shipitalo and Gibbs (2000) and Villholth and Jensen (1998). Both of these studies reported immediate breakthrough dominated by a few drain-connected macropores. Shipitalo and Gibbs (2000) observed the direct transfer of water from macropores to subsurface drains within 0.5 m on either side of the subsurface drain with a logarithmic relationship between infiltration rate and distance from the drain. Kumar et al. (1998) reported an express fraction in their work on atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) movement to subsurface drains but did not address this issue. An express fraction is not currently included in the distributed version of RZWQM.

Model Modification

The original macropore component of RZWQM routes the generated surface runoff downward through the macropore until it meets the water table. Lateral infiltration and mixing with soil surrounding the macropores can occur as water flows through the macropores. If water and chemical reach the top of the water table, then the water table is raised from this available water one layer at a time. As this available water is added to the layer immediately above the water table, the chemical is also mixed into that layer matrix. After mixing, the model raises the water table 1 cm and then fills the next layer until routing all the water. This results in a concentration bulge at the top of the water table as verified by the Br simulations.

The RZWQM model was modified by including a contributing area parameter relating the percentage of macropores in direct hydraulic connection to subsurface drains. When macropore flow first reaches the top of the water table, a macropore–subsurface drain express fraction (EF) of the water and chemical is routed directly into the subsurface drain through macropores. The EF is proportional to the available water and chemical that reaches the soil depth of subsurface drainage. The remaining water and chemical is allowed to fill and mix with the layers above the water table, as described above. The modified model routes water from a percentage of the macropores near subsurface drains directly into the drains to simulate macropore–drain connectivity. The EF will influence pesticide transport when there are macropores present and excess water is available on the soil surface during an infiltration time step. With this assumption, water will be available as an EF when water either reaches the drain directly (i.e., water table below subsurface drain) or the top of the water table (i.e., water table above subsurface drain). In the former, the macropore water front is decreased by the EF fraction and the remainder is added to the top of the water table. In the later, the macropore water front reaches the water table before the subsurface drain and then the model abstracts chemical as a continuous column of water above the subsurface drain that is instantaneously mixed and transported. This modification stems from the hypothesis that even if the average water table height is above the drain, macropore flow can occur directly into drains. The water table peaks halfway between drains and recedes to the drain depth at the drains. In cases where the soil matrix above the drains may be saturated for a short period of time because of capillary tension in soil, the macropores should still be open because the tension is very low in a 3-mm diameter macropore. Even if there is water in the macropore, mixing should allow flow from the surface directly into the subsurface drain.

The EF is input into RZWQM with the macroporosity parameters (soil physical property parameter). The EF is specified as the decimal percentage of effective macropores in direct connection with subsurface drains. Approaches that are more mechanistic are needed to derive EF but deterministic equations do not currently exist for analyzing macropore–subsurface drain connectivity as functions of soil and hydraulic conditions. Therefore, the model modification is an initial attempt to account for directly connected macropores and subsurface drains.

Bromide and ISO transport using the modified model were sensitive to EF, with greater subsurface drainage concentrations predicted as EF increased. Including an EF improved the response of the model in predicting immediate breakthrough of the tracer and pesticide. Model results with an EF = 0.02 or 2%, where the value of EF was determined by fitting the data to the measured Br concentrations, are presented in Fig. 3 and 4. An express fraction of 2% did not influence the simulated subsurface drainage. However, large values of EF will influence simulated drainage volumes. The first two simulated peaks in Br and first simulated peak in ISO matched the observed concentrations reasonably well. The modified model overpredicted ISO on Day 140. Predicted Br and ISO concentrations at Day 131 (i.e., the first peak) were 14.2 mg L^{-1} and 1.7 μg L^{-1}, respectively. A linear regression between predicted and observed Br and ISO concentrations resulted in slopes of 0.62 and 0.81, intercepts of 0.70 and 0.01, and R^2 of 0.43 and 0.60, respectively. The normalized objective functions after model modification were 0.7 for Br and 0.9 for ISO.

Fast breakthrough by drain-connected macropores mainly influenced initial breakthrough when concentration differences between the macropore and matrix flow domains were large. Therefore, simulated peaks in Br after Day 143 remained low compared with observed concentrations. The discrepancies in later peaks were the result of the model transporting more Br through the soil matrix as compared with measured concentrations. Consequently, less Br was available at the soil surface for transport through macropores during rainfall events. Figure 5a demonstrates that observed concentrations in the soil for depths between 0 and 15 cm match predictions by RZWQM. However, the model appeared to predict a Br wave or pulse through the soil profile as indicated by the increases in concentration in the lower soil layers (15–65 cm) as shown in Fig. 5b–d. Observed

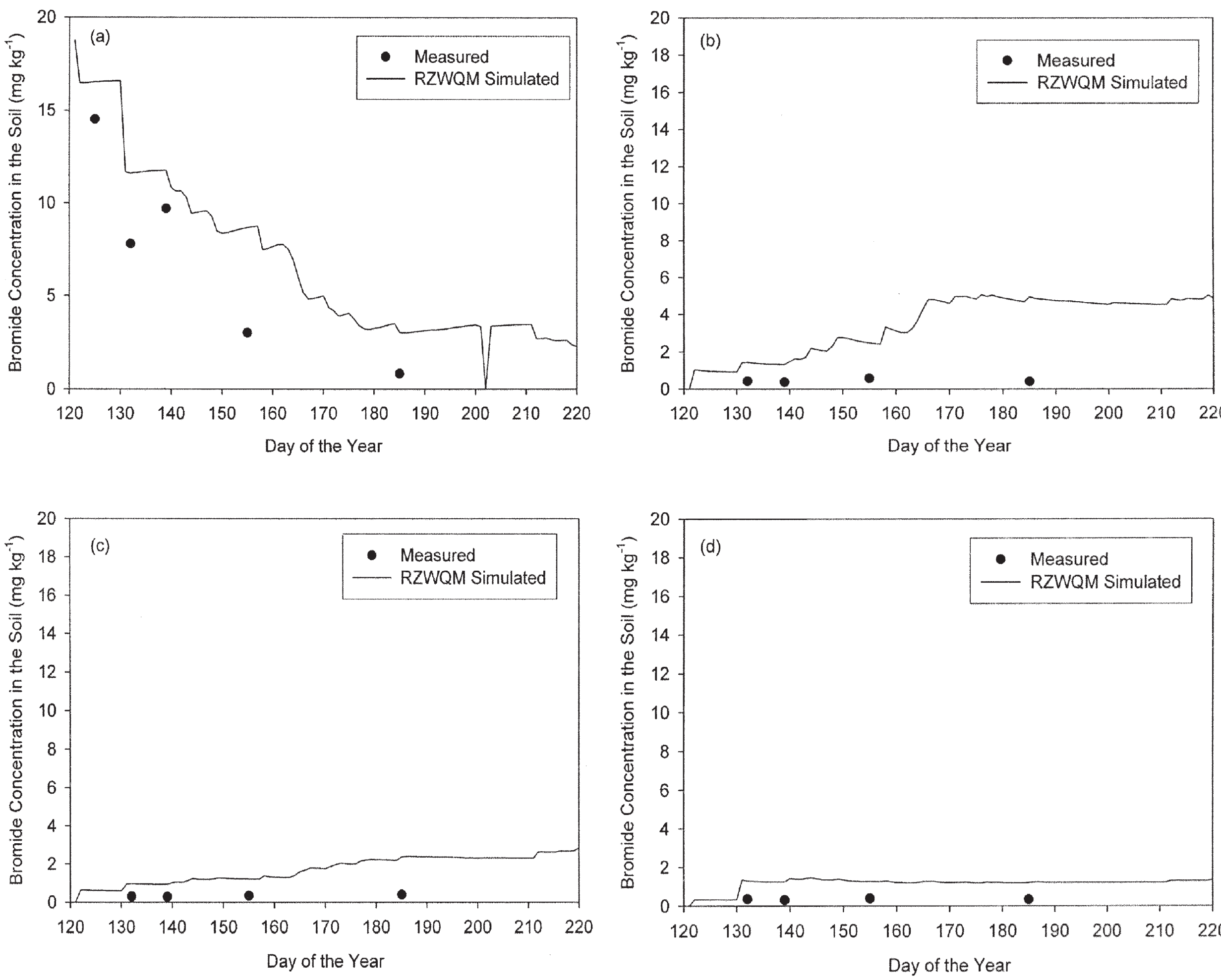


Fig. 5. Observed vs. Root Zone Water Quality Model (RZWQM) predicted bromide (Br) soil concentrations in the soil profile at depths (a) 0 to 15 cm, (b) 15 to 30 cm, (c) 30 to 43 cm, and (d) 43 to 65 cm.

data do not indicate such a concentration wave but a constant Br concentration between 15 and 65 cm below the soil surface. In fact, observed Br concentrations below the upper soil layer (0–15 cm) remained near 2 mg L^{-1} throughout the tracer study.

Therefore, the observed soil concentrations (along with the drain concentrations) suggest that most of the field Br remained in the surface mixing zone and is transported to drains through macropores. Possible hypotheses for this discrepancy include that Br may reside in surface residue or soil aggregates. Bromide may not be completely dissolving or a portion of the negatively charged Br may be adsorbing to the organic matter in the upper 2 cm of the soil profile. Isoxaflutole rapidly degrades and does not provide additional evidence to test these hypotheses.

CONCLUSIONS

The Root Zone Water Quality Model (RZWQM) was applied to a potassium bromide (KBr) tracer and isoxaflutole (ISO), the active ingredient in BALANCE herbicide, transport experiment at a field site in Allen County, Indiana. The model reasonably simulated the hydrologic response of the system with minimum calibration. However, the calibrated model failed to predict the early time response of Br and ISO movement into the subsurface drains. Recent research in macropore flow to subsurface drainage systems suggests such observations may be due to direct connection between macropores and subsurface drains. The direct connection between macropore flow and subsurface drainage was investigated in this research by modifying the macropore component of RZWQM to include an express fraction. The modified model simulated the early concentration peaks for both the conservative tracer and ISO.

In general, the modified model better represents the possible interrelationship between macropores and subsurface drains to capture early peaks in tracer and pesticide concentrations following application. Further research should be conducted to test the modified model under different climate, soil, subsurface drain configuration, and chemical applications. In addition, the degree of direct connectivity between macropores and subsurface drains needs to be characterized using approaches that are more mechanistic. A constant percent of macropore flow (e.g., 2%) directly entering drains is used in this manuscript. This is a very simplified assumption, and further investigation into directly connected macropores may indicate that the express fraction should change with varying saturated-unsaturated flow conditions above the tile drain. At this time, however, our understanding of the dynamics of the express fraction under different antecedent water content and rainfall intensities is insufficient.

APPENDIX

A_2	pore-size distribution index
C	coefficient relating the fall midway between the drains to the average fall of the water table
C_1	saturated hydraulic conductivity (m s^{-1})
C_2	second intercept on the conductivity curve
D_e	effective depth of the impermeable layer below the drain center (m)
f	drainable pore-space
h	matric suction head (cm)
K	saturated hydraulic conductivity of the soil (m s^{-1})
$K(h)$	unsaturated hydraulic conductivity (m s^{-1}) as a function of matric suction head, h (cm)
L	distance between the drains (m)
m_o, m_t	initial height and height at time t of the water table above drain centers midway between drains (m)
*macro**	volume of effective macropores per unit volume of soil (cm^3 cm^{-3})
N_1	first exponent on the conductivity
N_2	exponent for the conductivity curve
*nmacro**	number of effective macropores per unit area
NOF	normalized objective function
r_p	average macropore radius (cm)
S	bubbling pressure (cm)
STDD	standard deviation of differences
t	time (s)
x_i	i^{th} observed value
X_a	mean of the observed parameter
y_i	i^{th} predicted value
θ	soil water content (cm^3 cm^{-3})
θ_r	residual water content (cm^3 cm^{-3})
θ_s	saturation water content (cm^3 cm^{-3})

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